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Investigation of the Effects of Low-Temperature Non-Equilibrium Plasma Treatment

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***Abstract**:*

The article considers the issue of archaeological leather conservation with the application of new material treatment methods.

The work includes a microscopic examination of leather archaeological articles, a study of the microstructure of archaeological leather with various natural origins, and an identification of archaeological leather based on its generic origin.

The authors investigated of the influence of non-equilibrium low-temperature plasma treatment on the structural transformations of leather articles, and a study of its influence on the physical, mechanical and hygienic properties of archaeological leather articles prior to conservation.

Keywords: *Archaeological article, leather, low-temperature plasma, identification analysis, conservation, plastification.*

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1. Introduction

One of the most problematic art facts discovered at archaeological excavations are leather findings. It is accounted for by the characteristics of the behaviour of moist archaeological leather when it is exposed to air. In order to prevent drying and decomposition of the articles accompanied by destructive hardening of material, conservation procedures should be started from the moment when the articles are removed from the soil. Excavated archaeological leather is characterized by the following parameters: moisture, contamination, both surface and internal, deformation. Structural damaging of leather material by biotics – mould and fungi is frequently recorded (Richardin & Copy, 1994; Stambolov, 1969). Various techniques have been used in order to provide "first aid" to such artefacts (Elkina *et al.,* 1987; Waterer, 1972). For instance, Egyptian leather articles have been treated with the use of the laser cleaning procedure (Elnaggar *et al.*, 2011).

1.1 Polyethylene glycol conservation

Unfortunately, Russian scientific literature contains very few individual works related to the issue of archaeological leather conservation. The issue is actively studied by foreign restoration experts (Fogle, 1984). The leather conservation technique most commonly used in the Russian Federation which allows to restore leather articles close to their original appearance is based on the work of an expert restorer artist Sinitsina (Sinitsina and Solomatina, 2013).

According to this technique, leather conservation work starts with mechanical cleaning. Leather is cleaned with distilled water using art brushes with natural hair and soft flat brushes. At the next conservation step the article is submerged in a water and alcohol solution of low molecular weight polyethylenglycol (PEG400). The exposure of leather to this solution can be subdivided into two processes:

1. Diffusion. At this stage polyethylenglycol penetrates the interfibre spaces of leather tissue replacing water molecules.
2. Plasification. At this stage the leather tissue of the article restores its plastic properties.

After the exposure of archaeological leather to the water and alcohol solution of low molecular weight polyethylenglycol it is deposited for several weeks in a freezing chamber. Dry distillation of water from leather structure occurs at this stage due to low temperature without significant changes in the intermolecular space volume.

At the next stage leather is submerged in a different medium - a water and alcohol solution of high and low molecular weight polyethylenglycol (PEG). According to the technique by Sinitsina the process of submerging the article in a freezing chamber is repeated several times (Sinitsina and Solomatina, 2013).

The PEG conservation process is accompanied by paring of the flesh surface of leather tissue. This operation is performed manually with the use of a scalpel. The conservation process in considered completed when the leather tissue of the article obtains plastic properties.

The major advantage of polyethylenglycol consists in its ability to restore the physical and mechanical properties of leather tissue. However, the technique of PEG treatment of archaeological articles has a series of downsides:

- long duration of the conservation process;
- insufficient protective properties;
- lack of antibacterial properties.

The biggest disadvantage from the viewpoint of work performed by restorers and archaeologists is of course the long duration of the conservation process. All articles have individual properties, making it impossible to calculate an accurate time period by the end of which the article would acquire plastic properties in the PEG solution. The conservation period can vary from six months to over two years. This complicates the further restoration process and handling of the article by archaeologists. Considering the fact leather archaeological findings are quite rare, each item submitted for restoration has a great value as a cultural heritage object and a historical artefact studied by an archaeologist. Therefore, prolonged "termination" of operations with the finding significantly slows impedes the classification and systematization of excavated archaeological material, together with archaeological reporting.

2. Methods and Materials

The possibilities of using plasma modification within the existing restoration technique were studied in order to accelerate the conservation process. A low-pressure flow of plasma represents a high-frequency discharge. An article exposed to a flow of high-frequency (HF) plasma and reduced pressure becomes an additional electrode. Electrodes in an HFC discharge "swing" with respect to non-mobile ions under the influence of sign changes in an electric field. A flat sample submerged in low-temperature plasma splits an electron cloud into two parts each of which continues to "swing" with a certain ampitude. Thus, a layer of positively charged ions (PCI) is alternatively established on the opposite sides of the plate (Bulatova, 2001).

During low-temperature plasma treatment materials interact with active and inactive plasma particles having a high kinetic or potential energy. The effect of plasma on the material is achieved as a result of a series of complex interrelated processes of energy, mass and charge exchange between plasma particles and atoms of treated article (Rakmatullina, 2010).

An evaluation of the technological parameters of the plasma unit was conducted in order to assess the feasibility of using low-temperature plasma treatment for the purpose of improving the hydrophilic and physico-mechanical properties of archaeological leather. Archaeological leather fragments discovered at excavations of the island town of Sviyazhsk were used as test samples.

An identification analysis on the basis of the generic origin of raw materials was conducted as part of the study of these materials. Attribution of the generic origin of leather artefacts is suggested in a number of works (Brand *et al.*, 2014; Haines, 1984). The identification analysis of the archaeological leather in question is presented in several publications (Kulevtsov, Bogatova & Sepin, 2014; Bogatova *et al.*, 2016). Microphotographs of the leather tissue of archaeological articles dating back to various time periods were compared with the microphotographs of contemporary leather with different generic origins.

The type of animals whose skin corresponded to the archaeological findings was determined on the basis of microphotograph analysis results in accordance with (Haines, 2016). Most of the artefacts were made of leather crafted from sheepskin (Table 1).

Table 1: *The results of a study of the generic origins of raw materials used in the manufacture of archaeological leather materials.*

Type of raw tannery material	Quantity of archaeological artefacts
Cattle skin	5
Sheep skin	9
Goat skin	1

3. Experiment and Results

The articles were mechanically cleaned from contamination in order to determine non-equilibrium low-temperature plasma treatment modes. Then leather samples were subjected to non-equilibrium low-temperature plasma treatment. Prior to the conservation process the skins were processed in the following modes in order to impart hydrophilic properties: 1) gas: argon, p = 26.6 Pa, G = 0.04 g\s, U = 3 kV, I = 0.4 A, t = 5 min; 2) gas: argon (70)\propane-butane (30), p = 26.6 Pa, G = 0.04 g\s, U = 6 kV, I = 0.52 A, t = 5 min.

After plasma treatment of the samples the absorbability of a water droplet by leather surface was investigated. Figures 3-5 feature photographs of the shapes of water droplets on sample surfaces demonstrating the effect of plasma treatment on the shape of water droplets deposited on the front surface of leather upon application and after 15, 30 and 60 minutes.

A water droplet on the surface of the sample in the following mode: gas: argon, p = 26.6 Pa, G = 0.04 g\s, U = 3 kV, I = 0.4 A, t = 5 min, water is distributed across the surface upon application of a droplet. After 15 min the water droplet starts to dampen the sample surface (wetting angle 90 ºC). After 60 min the water droplet is almost completely distributed across the surface of leather samples. These study results confirm that hydrophilic properties are imparted during non-equilibrium low-temperature plasma treatment. Table 2 features the results of studying the influence of non-equilibrium low-temperature plasma treatment on leather archaeological articles prior to the conservation process.

An analysis of obtained experimental data confirmed (Table 2) that maximum cure temperature was demonstrated by leather samples treated with non-equilibrium low-temperature plasma in hydrophilic mode. Vapour permeability study results demonstrate that if the samples are treated with non-equilibrium low-temperature plasma in hydrophilic mode, their relative vapour permeability exceeds that of the untreated samples by 65 %, and that of samples treated in hydrophobic mode - by 39 %. It indicates that plasma treatment improves the hygienic properties of archaeological leather. The average cure temperature of these samples exceeds the reference values by 9 % and amounts to 49.2 °C. At the same time, the average cure temperature of leather samples treated with non-equilibrium low-temperature plasma in hydrophobic mode is 48 °C, which exceeds the reference value by 6.5 %. The results of the experiment are consistent with the results of studying primary physical and mechanical indicators.

Table 2: *Quality indicators of archaeological leather after non-equilibrium low-temperature plasma treatment.*

Quality indicators /Processing mode	Relative vapour permeability (%)	Tensile strength (MPa)	Wetting angle (O)	Tsv (°C)
Control	2.6	7.5	60.19	44.8
Hydrophilic	7.9	9.3	26.39	49.2
Hydrophobic	4.8	8.6	57.39	48

In order to determine the impact of the new process technique, the authors studied the microphotographs of archaeological articles before and after conservation and plasma treatment in hydrophilic mode. Examination of the front surface and cross-section of the article after conservation confirms the removal of contamination which could not be removed by mechanical cleaning. Ionized gas cleans not only the front surface of leather, but also the entire volume of material. It should also be noted that the netting structure of collagenic fibre bundles can be observed after conservation (Fig. 6). The plexiform and papillary layers can also be clearly observed.

4. Conclusions

It was concluded on the basis of the aforesaid results that non-equilbrium low-temperature plasma treatment can be used prior to the conservation of leather arcaeological articles. An optimal treatment mode has been determined to be the hydrophilic mode (gas: argon, p = 26.6 Pa, G = 0.04 g/s, U = 3 kV, I = 0.4 A, t = 5 min) (Bogatova & Kulevtsov, 2015).

The best results are demonstrated by samples treated by non-equilbrium low-temperature plasma in hydrophilic mode. Treatment of a sample by non-equilbrium low-temperature plasma in hydrophilic mode provides fibre separation in the leather tissue and the arrangement of pores across the entire volume of the sample. In turn, this effect provides a more homogeneous conservation process due to an increase of the diffusion of water solutions into the interfibre space.

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